(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 February 2001 (01.02.2001)

PCT

(10) International Publication Number
WO 01/07538 A1

(51) International Patent Classification[7]: C10G 45/64

(21) International Application Number: PCT/EP00/07178

(22) International Filing Date: 25 July 2000 (25.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99401906.5 26 July 1999 (26.07.1999) EP

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/07538 A1

(54) Title: PROCESS FOR PREPARING A LUBRICATING BASE OIL

(57) Abstract: Process for preparing a lubricating base oil by contacting a synthetic waxes, which wax is obtained by a Fischer-Tropsch process and has not been subjected to a hydroisomerisation treatment, with a catalyst composition comprising at least a hydrogenation component, dealuminated aluminosilicate zeolite crystallites and a low acidity refractory oxide binder material which is essentially free of alumina.

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PROCESS FOR PREPARING A LUBRICATING BASE OIL

The invention relates to a process for preparing a lubricating base oil from a hydrocarbon feed selected from a synthetic wax.

In the Fischer-Tropsch process a synthesis gas ($CO+H_2$) made, e.g., from natural gas, is converted over a catalyst, e.g., a ruthenium, iron or cobalt catalyst, to form a wide range of products inclusive of gaseous and liquid hydrocarbons, and oxygenates, and a normally solid paraffin wax which does not contain the sulphur, nitrogen or metals impurities normally found in crude oil. It is generally known that base oils can be obtained by catalytically converting the Fischer-Tropsch wax obtained from such process.

EP-A-776959 describes a process to prepare a base oil having a viscosity index (VI) of 151, a pour point of -27 °C and a Noack volatility of 8.8% by weight. The base oil was prepared by first subjecting a synthetic wax, also referred to as a Fischer-Tropsch wax, to a hydroisomerisation step. Subsequently the fraction boiling above 390 °C of the effluent of the hydroisomerisation step is catalytically dewaxed using a silica-bound surface-dealuminated ZSM-23 catalyst. US-A-5059299 describes a process to prepare a base oil having a pour point of -20 °C and a VI of 159 by first hydroisomerisation of the 390 °C+ fraction of a Fischer-Tropsch wax followed by solvent dewaxing.

US-A-5834522 describes a process in which a Fischer-Tropsch wax is first subjected to a hydrotreatment step in which unsaturated and/or oxygenated products present in the Fischer-Tropsch wax are removed. The hydrotreated product having a T10vol% of 258 °C and a T90vol% of

493 °C is subsequently subjected to a hydroisomerisation step and finally solvent dewaxed. The resulting base oil had a VI of 142 and a pour point of -21 °C.

EP-A-668342 describes the preparation of a base oil from a Fischer-Tropsch wax, in which first the Fischer-Tropsch wax is subjected to a hydrotreating step in which no isomerisation or cracking occurs. The hydrotreated effluent is subsequently subjected to a hydrocracking/hydroisomerisation step followed by a pour point reduction step. The pour point reduction step can be performed by means of solvent dewaxing, catalytic dewaxing or isomerisation dewaxing, also referred to as isodewaxing.

US-A-5882505 describes converting a Fischer-Tropsch wax by first subjecting the wax to a hydroisomerisation step followed by catalytic dewaxing. According to the specification the hydroisomerisation step is to provide base oils with good cold flow properties.

A disadvantage of the above described processes is that a multiple of reaction steps are required to obtain the final base oil product. The object of the present invention is a simple process which yields base oil products having a high viscosity index and a low pour point.

This object is achieved by the following process. Process for preparing a lubricating base oil by contacting a synthetic wax, which wax is obtained by a Fischer-Tropsch process and has not been subjected to a hydroisomerisation treatment, with a catalyst composition comprising at least a hydrogenation component, dealuminated aluminosilicate zeolite crystallites and a low acidity refractory oxide binder material which is essentially free of alumina.

It has been found that the Fischer-Tropsch wax can be converted to a base oil product having excellent

properties in one hydroconversion step instead of a hydroisomerisation step followed by a dewaxing step. Excellent properties are for example a pour point below -27 °C and a VI of above 140.

For the purpose of this description the synthetic wax is the fraction boiling above 350 °C of a product obtained by a Fischer-Tropsch process. The synthetic wax will also be referred to as the Fischer-Tropsch wax. The product directly obtained by the Fischer-Tropsch process will be referred to as the Fischer-Tropsch product. When reference is made to boiling points and boiling point ranges the boiling point at atmospheric pressure is meant.

The Fischer-Tropsch wax has an initial boiling point of above 350 °C. The congealing point of the Fischer-Tropsch wax is preferably at least 50 °C.

The Fischer-Tropsch process converts synthesis gas to a Fischer-Tropsch product comprising gaseous and liquid hydrocarbons and a Fischer-Tropsch wax. Synthesis gas is suitably prepared by gasification of natural gas, a hydrocarbon fuel or coal under known conditions. The Fischer-Tropsch product does not contain the sulphur, nitrogen or metal impurities normally found in crude oil, but is known to contain water, trace metals and a number of unsaturated compounds and oxygenate compounds such as alcohols, ketones, aldehydes, etc. A method to prepare a Fischer-Tropsch product is for example described in the afore mentioned EP-A-668342.

The Fischer-Tropsch product, including the wax, may have been subjected to a hydrotreatment process step in order to lower the content of these unsaturated or oxygenated products. These compounds may cause a deactivation of certain catalysts used in further downstream treatment of the Fischer-Tropsch product. In a hydrotreatment process step hydrogen is reacted with the

feed in the presence of a hydrotreatment catalyst. An examples of such a hydrotreating step is described in the afore mentioned US-A-5834522 and EP-A-668342. It must be understood that no or no substantial hydroisomerisation and/or cracking as illustrated in the above cited prior art takes place during such a hydrotreating step. For the purposes of this specification substantially no hydrocracking or hydroisomerisation is defined by that less than 10%, preferably less than 5%, of the fraction of the feed boiling above 370 °C in % by weight is converted to a fraction boiling below 370 °C.

If present, the hydrotreating step will be typically performed prior to the fractionation of the Fischer-Tropsch product into a Fischer-Tropsch wax and lower boiling fractions. These lower boiling fractions can be processed into valuable products by known processes as exemplified in some of the above referred to publications. In a preferred embodiment of this invention only the amount of the Fischer-Tropsch wax is removed from the Fischer-Tropsch product that is needed to prepare lubricating base oils. The remaining part of the Fischer-Tropsch product including the remaining part of the Fischer-Tropsch wax is sent to a hydroisomerisation step as defined above. The products thus obtained are fractionated and into valuable lower boiling fuel fractions, for example naphtha, kerosine and gas oil fractions.

Any lower boiling by-products and/or unconverted Fischer-Tropsch wax obtained in the catalytic dewaxing process according to the invention can suitable be routed to either the hydroisomerisation step or to the fractionator means here above described to further increase the overall yield to lower boiling fuel fractions.

The invention is also directed to a process to prepare a lubricating base oil as described above by performing at least the following steps:

(a) preparing a Fischer-Tropsch product by means of a Fischer-Tropsch process starting from synthesis gas,

(b) optionally hydrotreating the Fischer-Tropsch product in order to reduce the amount of unsaturated and oxygenated products,

(c) separating a Fischer-Tropsch wax from the Fischer-Tropsch product obtained in step (b) or (a),

(d) catalytic dewaxing the Fischer-Tropsch wax according to the process of the present invention thereby obtaining the lubricating base oil product.

Preferred embodiments of the above described process are apparent from the description and include embodiments in which lower boiling fuel products are prepared next to the lubricating base oil product. The lower boiling fuels are prepared starting from the Fischer-Tropsch product from which all or part of the Fischer-Tropsch wax has been separated from in step (c), which are subjected to an optional hydrotreating step (step (e)) followed by a hydroisomerisation step (step (f)) and a fractionation step (g).

The catalyst composition used in the present invention comprises a hydrogenation component, a surface dealuminated aluminosilicate zeolite crystallites and a low acidity refractory oxide binder material which is essentially free of alumina. Examples of such catalysts are described in WO-A-9641849.

The aluminosilicate zeolite crystallites preferably has pores with a diameter in the range of from 0.35 to 0.80 nm. This diameter refers to the maximum pore diameter. As is generally recognised, the pores in a molecular sieve are polygonal shaped channels having a minimum and a maximum pore diameter. For the purpose of

the present invention the maximum pore diameter is the critical parameter, because it determines the size of the waxy molecules which can enter the pores. Examples of aluminosilicate zeolites are aluminosilicates mordenite, zeolite beta, ferrierite, ZSM-11, ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-23, SSZ-24, SSZ-25, SSZ-26, SSZ-32, SSZ-33 and MCM-22 and mixtures of two or more of these.

Applicants have further found that a good base oil product can be prepared when a catalyst is used containing ZSM-12, preferably ZSM-12 having a low cristobalite contamination, more preferably containing less than 5 wt% cristobalite. Most preferably ZSM-12 crystallites are used as obtainable by crystallising a synthesis mixture including a source of silicon, a source of aluminium, a source of a cations, and an organic directing agent having the following general formula $(R^1R^2R^3N^+-X-N^+R^4R^5R^6)Y_2$, in which R^1-R^6 are organic groups, X is a bivalent aryl group and Y is a anion. It has been found that ZSM-12 crystallites having a reduced cristobalite content can be prepared in a relatively short crystallisation period with this process. An additional advantage is that small crystallites can be prepared in a practical manner by this synthesis method. The directing agent is preferably hexa-N-methyl-N,N'-p-xylylen-di-ammonium dihydroxide. The sources of silicon, aluminium and cations and the synthesis conditions can be those conventionally applied in the field of preparing aluminosilicate zeolite crystallites. Examples of possible cations are alkaline-earth ions like calcium, rubidium, sodium of which sodium is most preferred. Examples of silicon sources are fumed silica and silica sol. Examples of aluminium sources are aluminium hydroxide, aluminium isopropoxide (as obtainable from

Aldrich) and sodium aluminate. R is preferably an C_1-C_6 alkyl group of which methyl is most preferred.

When referral is made to ZSM-12 a zeolite having the MTW framework topology is meant. This class of zeolites includes CZH-5 as described in GB-A-2079735, Gallosilicate MTW as described in Y.X. Zhi, A. Tuel, Y. Bentaarit and C. Naccache, Zeolites 12, 138 (1992), Nu-13(5) as described in EP-A-59059, Theta-3 as described in EP-A-162719, TPZ-12 as described in US-A-4557919 and VS-12 as described in K. M. Reddy, I. Moudrakovski and A. Sayari, J. Chem. Soc., Chem. Commun. 1994, 1491 (1994)

The crystallite size of the aluminosilicate zeolite may be as high as 100 micron. Preferably small crystallites are used in order to achieve an optimum catalytic activity. Preferably crystallites smaller than 10 micron and more preferably smaller than 1 micron are used. The practical lower limit is suitably 0.1 micron.

The dewaxing catalyst composition used in the present process also comprises a low acidity refractory oxide binder material which is essentially free of alumina. Examples are low acidity refractory oxides such as silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these. The most preferred binder is silica. The weight ratio of the molecular sieve and the binder can be anywhere between 5:95 and 95:5. Lower zeolite content may in some cases be advantageous for achieving a higher selectivity. A higher zeolite content is to be preferred when a higher activity is desired.

The dealumination of the aluminosilicate zeolite results in a reduction of the number of alumina moieties present in the zeolite and hence in a reduction of the mole percentage of alumina. The expression "alumina moiety" as used in this connection refers to an

Al_2O_3-unit which is part of the framework of the aluminosilicate zeolite, i.e. which has been incorporated via covalent bindings with other oxide moieties, such as silica (SiO_2), in the framework of the aluminosilicate zeolite. The mole percentage of alumina present in the aluminosilicate zeolite is defined as the percentage of moles Al_2O_3 relative to the total number of moles of oxides constituting the aluminosilicate zeolite (prior to dealumination) or modified molecular sieve (after dealumination).

Preferably the surface of the zeolite crystallites are selectively dealuminated. A selective surface dealumination results in a reduction of the number of surface acid sites of the zeolite crystallites, whilst not affecting the internal structure of the zeolite crystallites.

Dealumination can be attained by methods known in the art. Particularly useful methods are those, wherein the dealumination selectively occurs, or anyhow is claimed to occur selectively, at the surface of the crystallites of the molecular sieve. Examples of dealumination processes are described in the afore mentioned WO-A-9641849.

Preferably dealumination is performed by a process in which the zeolite is contacted with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:

$$(A)_{2/b}SiF_6$$

wherein 'A' is a metallic or non-metallic cation other than H+ having the valence 'b'. Examples of cations 'b' are alkylammonium, NH_4^+, Mg^{++}, Li^+, Na^+, K^+, Ba^{++}, Cd^{++}, Cu^+, Ca^{++}, Cs+, Fe^{++}, Co^{++}, Pb^{++}, Mn^{++}, Rb^+, Ag^+, Sr^{++}, Tl^+, and Zn^{++}. Preferably 'A' is the ammonium cation. The zeolite material may be contacted with the fluorosilicate salt at a pH of suitably between 3 and 7. Such a

dealumination process is for example described in US-A-5157191. The dealumination treatment is also referred to as the AHS-treatment.

The catalyst composition is preferably prepared by first extruding the aluminosilicate zeolite with the binder and subsequently subjecting the extrudate to a dealumination treatment, preferably the AHS treatment as described above. It has been found that an increased mechanical strength of the catalyst extrudate is obtained when prepared according to this sequence of steps.

The hydrogenation component suitably comprises at least one Group VIB metal component and/or at least one Group VIII metal component. Group VIB metal components include tungsten, molybdenum and/or chromium as sulphide, oxide and/or in elemental form. If present, a Group VIB metal component is suitably present in an amount of from 1 to 35% by weight, more suitably from 5 to 30% by weight, calculated as element and based on total weight of support, i.e. modified molecular sieve plus binder. Group VIII metal components include those components based on both noble and non-noble metals. Particularly suitable Group VIII metal components, accordingly, are palladium, platinum, nickel and/or cobalt in sulphidic, oxidic and/or elemental form. Nickel and/or cobalt, if present at all, may be present in an amount in the range of from 1 to 25% by weight, preferably 2 to 15% by weight, calculated as element and based on total weight of support. The total amount platinum or palladium will suitably not exceed 10% by weight calculated as element and based on total weight of support, and preferably is in the range of from 0.1 to 5.0% by weight, more preferably from 0.2 to 3.0% by weight. If both platinum and palladium are present, the weight ratio of platinum to palladium may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5.

Catalysts comprising palladium and/or platinum as the hydrogenation component are preferred. Most preferred is when platinum is used as the sole hydrogenation component. The hydrogenation component is suitably added to the catalyst extrudate comprising the dealuminated aluminosilicate zeolite crystallites by known techniques.

Catalytic dewaxing involve operating temperatures in the range of from 200 to 500 °C, preferably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, preferably from 15 to 100 bar, more preferably from 15 to 65 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), preferably from 0.2 to 5 kg/l/hr, more preferably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil.

The invention will be illustrated by the following non-limiting examples.

Example 1

Synthesis of ZSM-12 (crystals between 15-20 μm):

The synthesis was performed with a 250 ml autoclave, which was properly cleaned before the experiments. A starting gel with a Si/Al ratio of 60. The chemical composition of the system was:

$$1.0\ NaOH : 1.0Q(OH)_2 : 0.166\ Al(OH)_3 : 10\ SiO_2 : 600\ H_2O$$

where Q is hexa-N-methyl-N,N'-p-xylylen-di-ammonium ($C_{14}H_{28}N_2$). The crystallisation was performed at 190 °C for 34 hours. The XRD analysis showed that a pure well-crystallised product is synthesised. No other crystalline phases were observed. The chemical analysis of the crystals showed a Si/Al of 62. SEM micrographs revealed

that very large crystals (15-20 µm along the c-axis) were obtained.

Example 2

The synthesis of smaller ZSM-12 crystals were also performed. To make the starting system more dense, the amount of template was decreased. In addition, 5 wt% as-synthesised ZSM-12 seeds, with respect to the silica content, were introduced into the starting gel. The chemical composition of the gel was :

1.0 NaOH : 0.75 R : 0.166 $Al(OH)_3$: 10 SiO_2 : 420 H_2O

where R is hexa-N-methyl-N,N'-p-xylylen-di-ammonium dihydroxide. The crystallisation was performed at 190 °C for 34 hours. The XRD analysis showed that a pure well-crystallised product is synthesised. SEM micrographs revealed crystal size to be about 1-2 µm along the c-axis. The zeolite crystallises as individual crystals which do not make complex aggregates. The chemical analysis of the small crystals showed a Si/Al ratio of 47.

Example 3

Preparation of the finished catalyst

A dealuminated, silica bound ZSM-12 catalyst (10 wt% dealuminated ZSM-12, 90 wt% silica binder) was prepared according to the following procedure. ZSM-12 crystallites as obtained in Example 1 were extruded with a silica binder (10% by weight of ZSM-12, 90% by weight of silica binder). The extrudates were dried at 120 °C. A solution of $(NH_4)_2SiF_6$ (45 ml of 0.019 N solution per gram of ZSM-12 crystallites) was poured onto the extrudates. The mixture was then heated at 100 °C under reflux for 17 h with gentle stirring above the extrudates. After filtration, the extrudates were washed twice with

deionised water, dried for 2 hours at 120 °C and then calcined for 2 hours at 480 °C.

The thus obtained extrudate was impregnated with an aqueous solution of platinum tetramine hydroxide followed by drying (2 hours at 120 °C) and calcining (2 hours at 300 °C). The catalyst was activated by reduction of the platinum under a hydrogen rate of 100 l/hr at a temperature of 350 °C for 2 hours. The resulting catalyst comprised 0.7% by weight Pt supported on the dealuminated, silica-bound ZSM-12.

Example 4

A Fischer-Tropsch wax which has been subjected to a hydrotreatment in order to reduce the oxygen content to below 500 ppmw as molecular oxygen, but which has not been subjected to a hydroisomerisation treatment having the properties as listed in Table I:

Table 1

Initial Boiling Point	337 °C
10 wt% point	432 °C
50 wt% point	483 °C
90 wt% point	529 °C
Final Boiling Point	575 °C

was contacted in the presence of hydrogen with the catalyst as obtained in Example 3 at an outlet pressure of 40 bar, a temperature of 388 °C, a WHSV of 1.0 kg/l.hr and a hydrogen gas rate of 700 Nl/kg. Gaseous components were separated from the effluent by vacuum flashing at a cutting temperature of 300 °C. The properties of the obtained lubricating base oil product and the yield of the catalytic dewaxing are given Table 2.

Example 5

Example 4 was repeated except that the dewaxing temperature was 390 °C and the hydrogen gas rate of

700 Nl/kg was used. The properties of the obtained lubricating base oil product and the yield of the catalytic dewaxing are given Table 2.

Table 2

product properties	Example 4	Example 5
yield calculated on feed (wt%)	45	36
viscosity at 40 °C (cSt)	21.52	21.14
viscosity at 100 °C (cSt)	4.832	4.724
VI	154	149
Pour Point (+/-1 °C)	-20	-32

Example 6

Example 5 was repeated at 345 °C with a dealuminated silica bound ZSM-12 catalyst (10 wt% dealuminated ZSM-12, 90 wt% silica binder), wherein the ZSM-12 crystallites were prepared as described in "Verified synthesis of zeolitic materials", volume 22 (1998), pages 644-645. The crystallite size range was between 10-100 nm. The catalyst was further prepared as described in Example 3. The yield as calculated on feed was 45 wt%. The viscosity at 40 °C was 20.67 cSt. The viscosity at 100 °C was 4,593 cSt. The VI was 143 and the Pour Point (± 1 °C) was -32 °C.

The above results illustrate that good quality lubricating base oil products can be prepared in a high yield by starting from a Fischer-Tropsch wax which has not been subjected to a hydroisomerisation step.

C L A I M S

1. Process for preparing a lubricating base oil by contacting a synthetic waxes, which wax is obtained by a Fischer-Tropsch process and has not been subjected to a hydroisomerisation treatment, with a catalyst composition comprising at least a hydrogenation component, dealuminated aluminosilicate zeolite crystallites and a low acidity refractory oxide binder material which is essentially free of alumina.

2. Process according to claim 1, wherein the hydrogenation component is platinum.

3. Process according to any one of claims 1-2, wherein the low acidity binder is silica.

4. Process according to any one of claims 1-3, wherein the aluminosilicate zeolite crystallites have pores with a diameter in the range of from 0.35 to 0.80 nm.

5. Process according to claim 4, wherein the aluminosilicate zeolite crystallites is of the MTW type.

6. Process according to claim 5, wherein the aluminosilicate zeolite crystallites is of the MTW type contains less than 5 wt% of a cristobalite impurity.

7. Process according to claim 6, wherein aluminosilicate zeolite crystallites is of the MTW type is obtainable by crystallising a synthesis mixture including a source of silicon, a source of aluminium, a source of a cation, and an organic directing agent having the following general formula $(R^1R^2R^3N^+\text{-}X\text{-}N^+R^4R^5R^6)Y_2$, in which R^1-R^6 are organic groups, X is a bivalent aryl group and Y is a anion.

8. Process according to any one of claims 1-7, wherein the dealuminated aluminosilicate zeolite crystallites are

obtained by contacting the zeolite crystallites with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:

$(A)_2/bSiF_6$

wherein 'A' is a metallic or non-metallic cation other than H+ having the valence 'b', preferably ammonium.

9. Process according to claim 8, wherein an extrudate of the aluminosilicate zeolite crystallites and the low acidity binder is contacted with the aqueous solution of the fluorosilicate salt.

10. Process according to any one of claims 1-9, wherein the lubricating base oil has a pour point below -27 °C and a VI of above 140.

11. Process to prepare a lubricating base oil by performing the following steps:

(a) preparing a Fischer-Tropsch product by means of a Fischer-Tropsch process starting from synthesis gas,

(b) optionally hydrotreating the Fischer-Tropsch product in order to reduce the amount of unsaturated and oxygenated products,

(c) separating a Fischer-Tropsch wax from the Fischer-Tropsch product obtained in step (b) or (a),

(d) catalytic dewaxing the Fischer-Tropsch wax according to the process as claimed in any one of claims 1-10, thereby obtaining the lubricating base oil product.

12. Process according to claim 11, wherein the remaining part of the Fischer-Tropsch product and part of the Fischer-Tropsch wax of the Fischer-Tropsch product which is not used in step (d) both obtained in step (c) and the unconverted Fischer-Tropsch wax obtained in step (d) is subjected to a hydroisomerisation step and the thus obtained hydroisomerisation product is fractionated into lower boiling fuel fractions.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/07178

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G45/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 765 209 A (INST FRANCAIS DU PETROL) 31 December 1998 (1998-12-31) claims 19,20,30 page 7, line 15 - line 20 page 10, line 16 - line 21 page 13, line 24 -page 14, line 4	1-3,8,9
X	WO 96 41849 A (SHELL INT RESEARCH ;SHELL CANADA LTD (CA)) 27 December 1996 (1996-12-27) claims 1-3,5-7,15,16,18 page 6, line 11 - line 19 page 11, line 3 - line 14	1-4,8,9
A	WO 97 12012 A (CHEVRON USA INC) 3 April 1997 (1997-04-03) claims 1,6 page 9, line 25 -page 10, line 9	1,2,11, 12

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
30 October 2000	07/11/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/07178

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 157 191 A (BOWES EMMERSON ET AL) 20 October 1992 (1992-10-20) cited in the application claims 1,2,4,12 column 10, line 26 - line 59	1,5,8,9
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

In. ational Application No
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